

Exposure controls the density of the silver image on the negative or print; the degree of development determines the contrast of the developed silver image. Thus, minimum exposure and a low-contrast silver image both favor fineness of grain, resulting in a more uniform appearance of the image of the lower densities of the print where graininess is most objectionable.

Graininess is the subjective sensation in an observer in response to the nonhomogeneity of the image. The result of the instrumental evaluation of the properties of an image that produces the subjective sensation of graininess is called granularity. Such an instrumental measurement eliminates the subjectivity of human observers and provides numbers that can be used to compare objectively the graininess of different photographic materials. Root-mean-square granularity numbers are now increasingly used for comparing the graininess of photographic films. According to R. A. Morris and D. H. Wait,<sup>106</sup> "Root-mean-square (rms) granularity is a measure of the spatial variation of density which is obtained when numerous readings are made with a microdensitometer. The square root of the arithmetic mean of the squares of these readings is the RMS granularity value." Morris and Wait found that the relationship of granularity to graininess was dependent upon the contrast and the density level of the image and the characteristics of the measuring instrument. They summarized their findings as follows:

1. the graininess of a print, where contrast and sharpness are constant, varies directly with the granularity of the negative;
2. increasing the print film contrast increases the graininess of the print by amplification of the negative grain;
3. increasing print film sharpness increases graininess of the print by better resolution of the negative grain; and
4. printer characteristics, relating to contact, specularity, and other factors affecting sharpness and effective contrast significantly alter the observed graininess of prints.

A more contrasty picture appears more grainy than a less contrasty one. Daan Zwick<sup>107</sup> studied the quantitative relationship between contrast and granularity, finding that an 8% change in gamma caused a 6% change in granularity. Zwick<sup>108</sup> found a critical density at which graininess was most objectionable in projected still and motion pictures. According to Zwick, "This density is relatively invariant with screen luminance, since it is relative to the adaptive white level of the picture. For color pictures this diffuse density is 0.9, including base and stain. For black-and-white images, measured diffusely, the value is 0.64. The difference between monochrome and color is due mostly to the Callier Q factor of silver images. For television display these values are displaced to 1.03 and 0.83, respectively." If granularity measurements are made at only one density, then such measurements would

be most meaningful if they were made at or near the values listed where graininess becomes most objectionable.

Graininess has been observed for some time to depend upon the nature of the photographic image, being most evident in areas of uniform, moderate density. Just-noticeable differences in terms of rms granularity for different color image content were studied by Daan Zwick and Daniel L. Brothers, Jr.<sup>109</sup> For a uniform image field around 1.0 density a 6% change in rms granularity was detectable as a graininess difference. For an average picture a 16% change in rms granularity was a just-noticeable difference. When the scene is very complex with much detail, a 30% change in granularity is needed to produce a just-noticeable difference. These values also apply as well to still and motion pictures, and probably also to the display of film on television.

Graininess—or its objective correlate, rms granularity—has been found to depend upon the contrast of the image. Low image contrast may be achieved by low-pH developing solutions, usually containing weakly activated developing agents and often with considerable amounts of silver halide solvents. Short developing times, even with more active developers, produce images with finer grain. The silver halide solvent in the developer etches the crystals in the emulsion layer, reducing the crystal size and influencing the size and form of the silver filaments produced by development. Some of the silver dissolved from the crystals may be deposited on the silver filaments, thickening them. For this reason a strong solvent, such as thiocyanate, is probably less desirable than a milder one, such as sodium sulfite. Strong solvent action also means a greater loss of emulsion speed. In *p*-phenylenediamine fine-grain developers the developing agent acts as a mild solvent, producing low-contrast images of extremely finely divided physically developed silver. This is achieved at the expense of a great loss in emulsion speed.

Fine-grain developers are often slow acting. Jones and Deisch<sup>105</sup> found that graininess appears not to be a function of the speed of development but rather to be related to the properties of the alkali used to activate the developing agent so as to shorten the developing time. Some developing agents may be thought to be grain producing, but the grain may be produced by the nature of the alkali needed to secure even weak development. Some alkalis, such as sodium hydroxide, appear to have a disintegrating action on the gelatin of the emulsion layer. This action gives the silver particles a greater chance to come together to form clumps, thereby increasing graininess. Developing agents requiring the stronger alkalis may become associated with the production of grain, even though some of this may be due to the action of the alkali.

Only underdevelopment was found by Philip A. Friedell<sup>110</sup> to decrease the coarseness of the image structure over that existing in the original emulsion. He reported that developers containing thiocyanate or similar agents produced a coarsening of the image structure, even with underdevelopment. Apparently, physical developing action was sufficient to thicken the silver particles. Sodium sulfite functioned primarily as an accelerator and did not significantly decrease image grain. Bromides and iodides in the developing solution, like thiocyanates and other silver halide solvents, had a detrimental effect on the image structure, suggesting that fine-grain developers should be used only once, as these halide ions are produced during film processing. Monroe H. Sweet<sup>111</sup> has stated, however, that used developing solutions produce finer-grain results than the more active fresh developer, even after increased time of development for the used solution. Friedell concluded that fine grain depended solely on the degree of development—that is, the extent to which the silver has been reduced. The finest grain was produced, according to Friedell, “with a normal developer coupled with suitable overexposure of the film with development carried to a degree where a *negative printable on the hardest grades of paper only*, is produced.” The use of contrasty paper for the print will emphasize graininess, so that some of the fine-grain characteristics of the negative may be lost.

A compromise must be made between the degree of development or contrast of the film material and the degree of contrast of the photographic paper of the print. J. I. Crabtree<sup>112</sup> has said that it is better to develop a negative to a low gamma and make the print on contrasty paper than to produce a higher-contrast negative and make the print on softer paper. Because fine-grain development often involves the action of low-activity developers, these solutions are particularly sensitive to the effects of use: reduction of activity through exhaustion of the developing agents; the increasing restraint of the buildup of bromide and iodide in the solution resulting in a loss of shadow detail; and an accumulation of gelatin, dirt, and other foreign matter that may degrade the image upon enlargement. For these reasons a developer used once, then thrown away, is ideally suited for consistently maintaining the highest quality, fine-grain production.

Although the effect of processing conditions has not produced a consensus concerning the optimum film treatment, it is generally felt that the wet time of processing should be as short as possible. If the photographic material with the finest-grain emulsion is chosen, a more rapid-acting developer may be used, shortening the development time, and yet fine grain is achieved by the inherent characteristics of the photographic material. A 30- to 60-sec wash in running water rather than an acid stop bath is suggested to follow low-pH developers. A rapid fixing bath will speed up this time-consuming step to be followed by the minimum wash time. All processing solutions, including the

wash water, are at essentially the same temperature to minimize swelling variations of the emulsion layer in the various liquid baths. A few seconds treatment in a wetting solution should be followed by drying at room temperatures, but long-time drying under humid conditions should be avoided.<sup>113</sup>

The conditions most suitable for fine-grain development have been summarized in the preceding paragraph, but it should be noted that there is no absolute agreement between various investigators. Jones and Deisch failed to note any difference in image graininess when a pyrogallol developer was used at 15, 20, 25, or 30°C. The addition of considerable concentrations of potassium bromide to the pyrogallol developer failed to show any appreciable effect on the graininess of the strips, nor did the use of an acid fixing bath following the alkaline developer.

A. Marriage<sup>114</sup> reported the lack of effect of processing conditions upon image structure. Arthur C. Hardy and Loyd A. Jones<sup>115</sup> stated that “the fixing, washing and drying conditions were found to have no effect on graininess.” The rate of drying had no effect in the studies of F. L. English.<sup>116</sup> As is often true in photographic processing, the individual processor often has to determine the validity of the prescribed recommendations to his own operating procedures and photographic materials.

Modern concepts of securing fine-grain development are based primarily on the nature of the photographic emulsion, with carefully selected grain size and grain distributions contained in thin, compact emulsion layers. R. B. Willcock<sup>117</sup> has said, “The solution of the fine grain problem will doubtless be found in newer emulsions, not in the rearrangement of old [developer] formulas; for that reason it is wisest to make the best of what we have available and wait.” This was said in 1936.

For those of today's photographers who cannot wait any longer for the ultimate in fine-grained emulsions, possibly following Lloyd E. Varden's “Five Factors for Fine Grain” would be the best course.<sup>118</sup>

*First*—Select a film as slow and of the finest grain as the conditions of exposure and development permit.

*Second*—Expose the film properly but not more than is necessary to record the amount of shadow detail desired.

*Third*—Develop the film in a suitable fine-grain developer in which as much film speed as possible is assured.

*Fourth*—Develop the film to a gamma of about 0.7 [or less] as approximately indicated by time-temperature tables.

*Fifth*—After complete fixation and washing in solutions of the same temperature as the developer (preferably 65°F), dry the film normally in a warm current of dust-free air.

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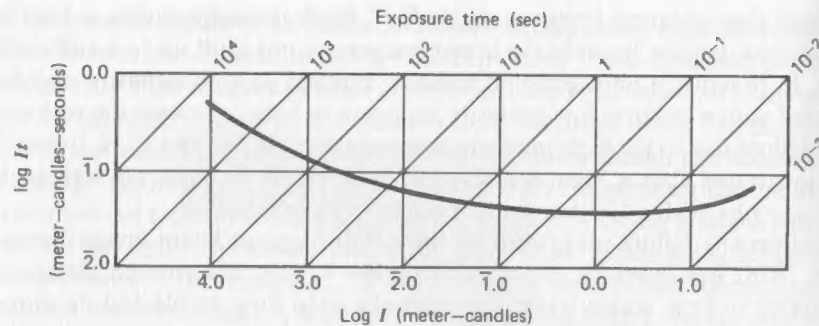


Figure 16. Graph showing reciprocity-law failure. [Eastman Kodak Company]

probably the first to study the effect quantitatively. Abney noted that an intermittent exposure was less efficient in forming latent image than a continuous exposure of equal energy. The exact effect depended upon the intensity of the exposing light, the number of separate flashes, and the ratio of the length of the light to dark periods.

Many investigators have studied the intermittency effect because of its importance in the design of a sensitometer, an instrument for exposing photographic materials for scientific study. The intermittency effect is often associated with the production of less density than that given by an equal-energy continuous exposure. More recent studies<sup>32</sup> have shown that when the light intervals of the intermittent exposure are about equal to the average rate of incidence of the photons upon the silver halide crystals, the intermittency effect disappears; that is, the intermittent exposure yields the same density upon development as would a nonintermittent exposure of the same duration and average intensity.

Intermittent exposures may form more density than an equal-energy continuous exposure when a sufficiently high intensity of illumination is used. At lower intensities a loss in density resulted. The gain or loss, or zero effect, of image density by intermittent exposure was explained by Raymond Davis<sup>33</sup> in the following manner:

After extinguishing the illumination the latent image is subject to modification by two opposing influences, one tending to intensify it, the other to fade it—both rapidly decreasing with time. At the higher illuminations the resultant effect is a growth in density; at the lower, fading results. When the exposure is intermittent each interruption adds a part to the total growth or diminution of the image, but it is readily appreciated that, as the rest periods shorten, the change introduced by each interruption should diminish. Consequently, there should be a limit to the modification which an increase in the number of interruptions can cause.

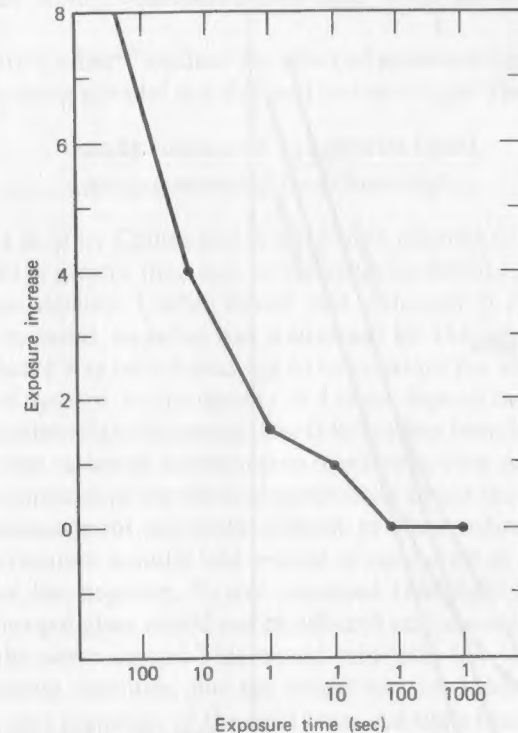


Figure 17. Reciprocity failure of Kodak Royal-X Pan film.

Intermittency failure is in the same direction as reciprocity failure but of a lesser magnitude. The loss of density given by the intermittency effect is associated with the underexposure region of the  $D$ - $\log E$  curve. In this region the curve produced by a continuous exposure rises more rapidly than the curve produced by an intermittent exposure. It was found by Clarence E. Weinland<sup>34</sup> that previous exposure to bring the latent image up to the beginning of the straight-line portion of the curve caused almost complete elimination of the intermittency effect. (See Figure 18.)

Reciprocity failure, and the associated intermittency effect, has significance for both the photographer and the scientist. At one time sensitometers used a constant-intensity light source that was modulated by a rotating sector wheel to vary the exposure. Because of the significant reciprocity failure that may be involved in such an exposing technique, this type of sensitometer has largely been supplanted by a sensitometer that is moderated in intensity by a continuous wedge or stepped tablet of varying densities. The exposure is

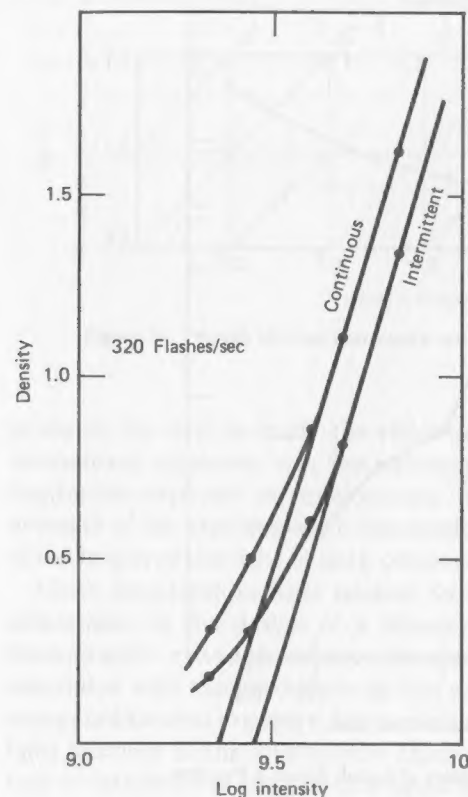


Figure 18. Characteristic curves with continuous and intermittent exposure, as determined by Clarence E. Weinland.<sup>34</sup>

continuous and of the same duration throughout the range of densities of the wedge or tablet.

### The Measurement of Density

The density of the silver image is not an absolute quantity but depends upon the method of measurement of the opacity. The silver image of a negative is composed of fine particles of metallic silver which both absorb and scatter light passing through the negative. A portion of the incident light may pass directly through the negative. W. de W. Abney engaged in considerable controversy with F. Hurter and V. C. Driffeld in the early 1890s concerning the value of various instruments to measure transmitted light.<sup>35-38</sup> Chapman Jones<sup>39</sup> later (1898) showed that scattered light could cause considerable discrepancies in the measurement of density, and that it was the scattered

light that made Abney's measurements differ from those of Hurter and Driffeld.

In 1909 Andre Callier<sup>40</sup> studied the effect of scattered light upon density measurements, using parallel and diffused incident light. The ratio of

$$\frac{\text{density (measured by specular light)}}{\text{density (measured by diffused light)}}$$

was designated as  $Q$  by Callier and is often now referred to as the Callier  $Q$  factor.  $Q$  is always greater than one, as the specular density is always greater than the diffuse density. Callier found that although  $Q$  differed for each photographic material, its value was a constant for the density range of his work. The  $Q$  factor was later found not to be constant for all densities but to be a function of density. As the density of a silver deposit increases, the scattering of the incident light increases. The  $Q$  factor has been found to increase rapidly at the low values of density up to maximum, then decrease slowly.<sup>41</sup>

Because the amount of the silver deposit determined the amount of light scatter, the measurement has been difficult to standardize. Early density-measuring instruments usually had a sheet of opal glass in contact with the silver image of the negative. It was reasoned that light that was totally scattered by the opal glass would not be affected very much by the additional scattering of the silver image. This would minimize the variations of light scatter by different densities, but the values obtained depended upon the color, quality, and thickness of the opal glass. All light that passed through the photographic material should be measured. This was the conclusion of A. J. Bull and H. Mills Cartwright,<sup>42</sup> who proposed to use a hollow white sphere, called an integrating sphere, as a collector for all the light that was transmitted through the photographic material.

Density measurements by different instruments often produced different results. It would be desirable to have one method to yield standardized results so that densities could be compared throughout the world. A. M. Koerner and Clifton Tuttle<sup>43</sup> suggested that

The necessary means for measuring the whole of the fluxes is available in the form of the integrating sphere. This device comprises simply a hollow, thin-walled sphere into whose periphery have been cut a pair of windows, located at approximately 90° from each other, and whose interior has been surfaced with some highly reflective and highly diffusive material such as magnesium oxide. Dimensions are immaterial, so long as the area of the apertures remains a negligible fraction of the whole surface of the sphere. It has been shown in the literature that the brightness of the interior of the walls of such a sphere is directly proportional to the amount of flux entering through the aperture, regardless of direction. Hence, if light from an external source is allowed to enter through one of the openings, the flux incident at the opening can be determined

diffusion factor

by observing, through the second aperture, the brightness of the wall. If now a photographic image is laid against the first aperture and a second observation is made, all of the flux transmitted, either specularly or in a scattered manner, by the image, will have been determined, and by applying the Hurter and Driffield equation a value for the density of the image can be arrived at.

The integrating sphere of a density-measuring apparatus may measure all the incident light and all of the transmitted light, but the values obtained still depend upon the nature of the incident light. Practical density measurements may involve scattered (diffused), parallel (specular), or a combination of these two kinds of incident light. (See Figure 19.)

Three distinct kinds of density measurements are possible:

1. *Double diffuse density.* The incident light is diffuse, not specular, in nature. The measuring device is an integrating sphere that is in contact with the silver image. All the transmitted light, both scattered and unscattered, is measured.
2. *Diffuse density.* Essentially parallel rays of light are used to illuminate the silver image. As with doubly diffuse density measurements, the light collector measures all transmitted radiation. When a negative is placed in contact with a sheet of photographic paper and near parallel light is used to make an

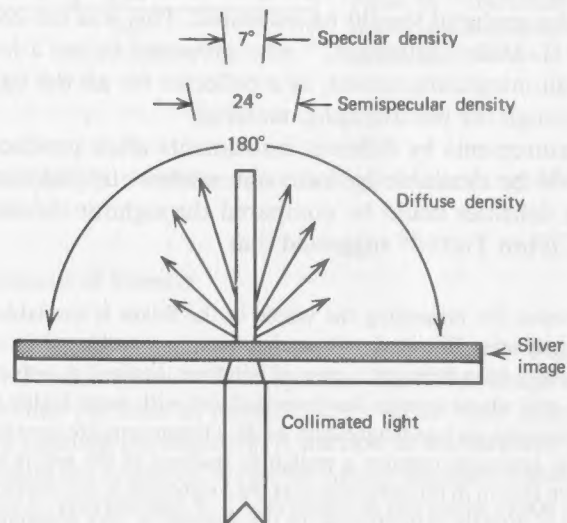


Figure 19. Means of collecting light after passing through a silver photographic image for making density measurements. [Eastman Kodak Company]

exposure, these photographic conditions of contact printing approximate the use of diffuse density of the silver image of the negative.

3. *Specular density.* When the light collector of the densitometer is moved back from the negative, only the direct rays of the light will be measured when the negative is illuminated with specular light. The incident light that was scattered will not be detected by the collector because the scattered light will diverge past the opening of the integrating sphere. Some of the incident light, though passing through the silver image, will not be detected by the densitometer. The amount of detected light will be less than the transmitted light, and the specular density will be higher in value than if both the scattered and direct light (totally diffuse density) were measured.

In projection printing with an enlarger having nearly parallel light (light collimated by condensers), the light emerging from a negative will consist of scattered and direct radiation. The light detector—the photographic paper—is at some distance from the negative, however, and the photographic emulsion will be affected primarily by the specular component of the transmitted light. The effective density of the photographic silver image is different for contact and projection printing because only part of the transmitted light is used for projection printing. Because the scattered light is not as effective with projection printing as it would be with contact printing, the contrast of the projection print will be higher than the contrast of the contact print, even though the same incident light illuminated the same negative in both methods of print making.

The density of the silver image of a photographic print is measured by reflectance. In this case the surface gloss plays an important part. If the silver image is illuminated with light at 45 deg to the print surface and the light detector is perpendicular (at 90 deg) to the surface, the effective reflection density will be measured. When the light detector is at 90 deg to the incident light, the specular reflection density will be measured. The total reflection density would be found by measuring the total light reflected in all directions and comparing the quantity with that of the incident light.

### Covering Power

The efficiency of exposure is expressed in terms of density when the  $D$ -log  $E$  curve is constructed. But the amount of metallic silver in different photographic images may vary considerably, even though the images may have the same optically measured density. A measure of the efficiency of the metallic silver of an image to produce light-stopping opacity is called the covering power of the silver. Covering power is calculated by dividing the



grams of silver in a square decimeter of the original photographic material into the developed density given by that silver coverage; that is,

$$\text{covering power} = \frac{\text{density}}{\text{silver (g/dm}^2\text{)}}$$

The inverse of this relationship—the mass of silver divided by the density that it has produced—has been termed the photometric constant. Covering power, rather than its inverse, is now commonly used to study the conditions that produce maximum image blackness for the minimum amount of image silver, an obvious and desirable goal as the world's supplies of silver become less plentiful. Covering-power values depend not only on the properties of the silver deposit but also upon the method of measuring the density.<sup>44</sup>

Covering power is influenced by many factors. In 1928 S. E. Sheppard and A. Ballard<sup>45</sup> pointed out that covering power decreased with the time of development. This decrease was attributed to the increase in the average size of the developed silver particle with time of development. Many small silver particles of low mass are much more efficient than larger particles with relatively high mass per particle. Covering power was also found to increase with increased exposure, presumably by the selective action of exposure upon the larger silver halide crystals, which are more light-sensitive. Fog silver is much less effective (has lower covering power) in light-stopping action, and such silver may have a covering power only one-fifth that of silver formed by exposure and development. Even when all the silver halide in a film was developed to fog silver, the density of the maximum fog was much less than the maximum image density.<sup>9</sup>

Recent studies have indicated that the number of silver particles per unit area, their distribution in the emulsion layer, and their light-scattering and absorption characteristics primarily determine the density given after development of an ordinary emulsion layer. The interaction between exposure and development was summarized by G. C. Farnell and L. R. Solman<sup>46</sup> as follows:

A fully chemically-developed silver-halide grain is a mass of silver filaments. The size of this mass, for a given size of silver halide grain, depends on the conditions of exposure and processing and also on certain properties of the emulsion. If the exposure is such as to produce large numbers of latent-image specks on each grain, e.g., a heavy high-intensity exposure, the developed grain may be very similar in size and shape to the undeveloped grain. With a low-intensity exposure producing only one or two latent-image specks, the developed grain is usually irregular in shape and larger than the undeveloped grain. Consequently, CP [covering power] may be higher for a low-intensity than for a high-intensity exposure.

Processing conditions play a vital role in determining the covering power of a developed silver image. The type of the developer, chemical or physical, influences the density given by the metallic silver, as the common non-filamentary silver particles given by physical development usually have less light-stopping power than the tangled mass of filaments given by chemical development. After the first stages of development in solution physical developers, the covering power of the developed silver decreases and the image becomes less neutral in color as the relative amount of solution physical development increases.<sup>47</sup> If the image is not neutral spectrally, covering power will depend to a degree on the wavelength of the light used to determine the image density.

The dependence of the covering power of the developed silver on the temperature and composition of the developer was studied by T. H. James and L. J. Fortmiller.<sup>47</sup> They reported that

During development, filaments may extend beyond the boundaries of the silver halide grain, providing the gelatin layer surrounding the grain can be readily penetrated. Swelling and softening of the gelatin would favor this penetration, whereas hardening would tend to prevent it. Accordingly, for a given degree of development, the filamentary silver formed by development of a given grain is less compact when the degree of swelling and softening of the gelatin is greater. Increased temperature promotes softening and swelling in the emulsions which have not been excessively hardened. Microscopic observations showed that the developed grains formed at the higher temperatures actually are larger, and hence have a less compact filamentary structure, since the mass of the silver is the same. The amount of gelatin washed out of the emulsion layer during processing also may be an important factor. An irreversible loss of density upon drying of a processed emulsion occurs with many materials, and this can be attributed to a compression of the filamentary structure by the contracting gelatin. The measurements made by Berry on the pressure exerted by the dry gelatin on the silver filaments suggest that the compression forces are weaker in the emulsion layer developed at the high temperature. The weaker force may be the result of the wash-out of part of the gelatin or may be associated with some other change occurring in the gel structure during the high-temperature development.

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manufacture of colour materials. The idea has naturally been considered, of mixing the three emulsions, differentially sensitized and associated with their respective couplers, to simplify the process. If the mixing is directly carried out in gelatin, however, it becomes impossible to restrict the action of the different silver halides towards their respective couplers.

The difficulty is overcome by dispersing each colour sensitized emulsion, together with its colour coupler, in an appropriate medium. This medium can be a non-volatile liquid or a dispersible polymer.<sup>(76)</sup> Three silver chloride emulsions, respectively sensitized to blue, green and red, and containing yellow, magenta and cyan couplers can be protected in this way and mixed in a solution of gelatin or other colloid as fine particles. Preferably, each emulsion should be dispersed separately in the colloid before mixing. In addition, to prevent diffusion of developer oxidation products from one particle to another, it is suggested that a grainless silver iodide emulsion containing a non-coupling reducer should be added to the mixture.<sup>(77)</sup>

These mixtures of emulsion and coupler are used for the manufacture of single layer colour papers.

## COLOUR DEVELOPERS

### 554. Colour developers containing coupler

To develop the latent image of a silver halide emulsion to colour, the developer should contain both a substituted p-phenylenediamine and a coupler (or former). The bath generally contains an alkali carbonate and a relatively small amount of sodium sulphite.

The coupler is usually dissolved first in a water miscible *organic solvent*: methanol, ethanol, isopropyl alcohol, acetone. With the naphthols, the sodium salts can be prepared with caustic soda.

We have seen that the colour produced depends mainly on the choice of coupler and to some extent is influenced by the particular p-phenylenediamine. The formularies advise the following compounds, but many others exist, which are often superior, and which have been given in this chapter.

*Cyan couplers*: 1-naphthol, 2:4-dichloro-1-naphthol, m-hydroxybiphenyl.

*Magenta couplers*: p-nitrophenylacetonitrile, 1-phenyl-3-methyl-5-pyrazolone.

*Yellow couplers*: acetanilide and its derivatives, particularly acetoacet-2:5-dichloranilide.

*Colour factor*. This is the ratio of dye/silver. It does not have a constant value as it varies with the development time and with the density of the silver image. As we have seen, the reduction of the silver image and the formation of the dye do not take place simultaneously, and consequently do not follow

equimolecular proportions of developer and coupler are present (greatest independence of colour factor compared with the silver density).

Tull has shown that the coloration factor decreases as the colour density increases, the variation being more accentuated when development is too rapid. The phenomenon is most apparent when the coupler concentration is too low, or the sulphite too high.

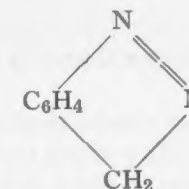
*Sulphite concentration*. Colour development takes place even in the absence of sulphite. According to Evans and Hanson, the latter's role is played by the coupler. In the absence of sulphite, the colour factor increases greatly. With too high a sulphite concentration, the colour curve falls below that of the silver, whilst the opposite is true with the normal developer.

The pyrazolones are the couplers which are most sensitive to variations in sulphite concentration.

*Alkali content*. An increase in the amount of alkali increases the activity of the bath and the speed of development, but also increases the tendency to oxidize, and hence the fog. Jelley has recommended the replacement of alkali by an alkylamine such as triethanolamine whose solvent action is less than that of ammonia.<sup>(78)</sup>

The anilides and the nitriles are susceptible to variations in pH.

*Anti-foggants*. Development fog can be avoided by adding an organic anti-foggant to the developer. The use of a nitro or amino *indazole*<sup>(79)</sup> has been particularly recommended, for example 1-methyl-5-nitro-indazole at a concentration of 0.2 per 1000.



### 554b. Colour developer formulas

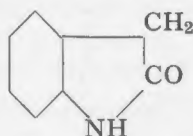
These are of the following general type:

Water to	1000 cc
Sodium sulphite anh.	5 g
Diethyl-p-phenylenediamine hydrochloride	3 g
Potassium carbonate	60 g
Potassium bromide	2 g
Coupler	1 g
Acetone or alcohol	50 cc

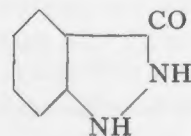
P4503

of the resulting ethyl- $\beta$ -  
d Itano obtained it in  
l being eliminated with  
sulphophenyl-, bromo-  
a benzoylamido, nitro-  
o (see para. 540). With  
similar to the following

*Other heterocyclic magenta couplers.* These include, chiefly, the *oxindoles* and the *indazolones*:<sup>(36)</sup>



Oxindole



Indazolone

In the case of the indazolones the link with the p-phenylenediamine is *via* the middle NH group. The benzene ring can have a chain such as  $R'R^2N.SO_2-$  in the  $\beta$ -position (to the CO) (I.C.I.: F.P. 1,089,328 Brit. prior. 1952).

Magenta couplers derived from *quinoline* have been patented by General Aniline (F.P. 939,497 U.S. prior. 1947 and Add. 61,004 and 61,006; 1954) with: in position 2, an alkyl, aminophenyl, stearylaminophenyl, octadecane-sulphonamidophenyl group; in position 4, a COOH or CONHR group; in position 6, a sulphonated aliphatic radical containing at least 10 carbon atoms and an OH in position 8. There are many variations.

tion by a  $-CH_2-$  or  
gs (Du Pont) and by  
(34) Some simple pyra-



roups substituted. Dye  
on 3 is an aminohetero-  
n patented by Kodak

n the CO and the neigh-  
amino-pyrazo-coumara-  
and ethyl  $\beta$ -amino- $\beta$ -

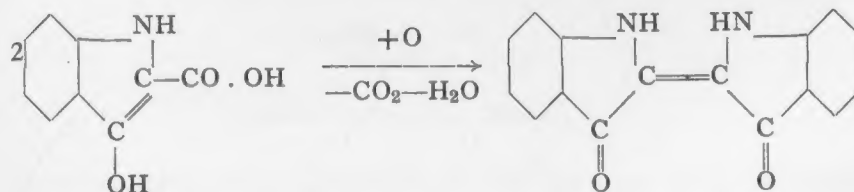
### 539. Other colour coupling systems

The direct formation of colour images by development does not necessarily involve the presence of two reagents. There are systems in which the developer, by simple oxidation produces a coloured substance *in situ*.

In this way *pyrocatechin* and *pyrogallol* in the absence of sulphite, produce, in addition to the silver image, a residual brown organic image which tans the gelatin strongly.

The following systems which can be used for the production of colour images are of greater interest:

*A. Indigo derivatives.* *Indoxyl* and *thioindoxyl* are respectively oxidized to the blue *indigo* and the magenta *thioindigo*. They are the basis of the discovery of colour development by Homolka. Their acid derivatives bring about the same result more easily:



Indoxyl-carboxylic acid

Indigo (blue)